



Optical and electrical properties of thermally evaporated ZnSe thin films

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Abstract : Zinc Selenide (ZnSe) thin films were deposited onto glass substrates by thermal evaporation technique. From optical studies, different optical constants were calculated and the transition of the deposited films were found to be direct allowed transition. The optical band gap of the films were found to be in the range from 2.6eV to 2.7eV. The films deposited at elevated substrate temperature followed by heat treatment in vacuum have showed stable electrical nature. The electrical conductivity of the ZnSe films were found to be about 10^{-7} ohm⁻¹ cm⁻¹ and found to increase to about 10^{-5} ohm⁻¹cm⁻¹ when films were doped with Al or Cu. From the conductivity measured at different temperatures, the activation energy of the films were calculated and found to be between 0.1 eV to 0.2 eV for low temperature regions and between 0.5 eV to 0.6 eV for high temperature region.

Keywords : Thermal evaporation, optical constants, optical band gap, electrical conductivity, activation energy

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1. Introduction

Zinc selenide (ZnSe) is one of the II-VI semiconductors that have been studied intensively in recent years. This fact is due to its direct and wide band gap. It is suitable candidate for the solar cells, blue laser diode, light emitting diode, thin film transistors and other optoelectronic devices. A variety of methods for preparation of ZnSe films have been reported by different authors like chemical vapour deposition, electrodeposition, photochemical deposition, pulsed laser deposition and vacuum evaporation [1-5]. Electrical and optical properties of semiconducting films are essential requirement for proper application in optoelectronic devices, and these properties are very sensitive to deposition conditions and technique used. In this paper some optical and electrical properties (transmission and

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spectra, absorption coefficient, refractive index, extinction coefficient and electrical conductivity) of ZnSe thin films deposited by thermal evaporation method have been reported.

2. Experimental

ZnSe thin films were prepared by thermally evaporating ZnSe polycrystalline powder (99.99% purity) under vacuum, at a pressure of less than 10^{-5} Torr onto chemically cleaned glass substrates placed at a distance of approximately 8 cm from the vapour source. During deposition of the films the substrates were kept at different elevated temperatures. The prepared films were annealed in vacuum at higher temperature for one hour. For preparation of Al-doped and Cu-doped films, the pure metal Al or Cu was co-evaporated along with ZnSe and then the films were annealed at a temperature of 350°C in vacuum. X-ray diffraction patterns of the samples were taken by using Cu K α radiation. The thickness of the films were measured by the multiple-interference method developed by Tolansky [6] and were in the range between 180 and 380 nm. Transmission spectra were obtained using a UV-VIS spectrophotometer (Carry 300, Varian), at room temperature. All electrical measurements were done in vacuum under pressure of 10^{-2} Torr using a rotary pump. The currents were measured with the help of a system electrometer (6514, Keithley). The details of experimental arrangement was given else where [7].

3. Results and discussion

3.1 Structural property:

The x-ray diffraction study of ZnSe films prepared at higher temperature indicates (Figure 1) that the samples are polycrystalline and have a cubic zincblende structure. The crystallites are preferentially oriented with the (111) planes parallel to the substrate. However, as deposited ZnSe films deposited at room temperature show amorphous in nature. The

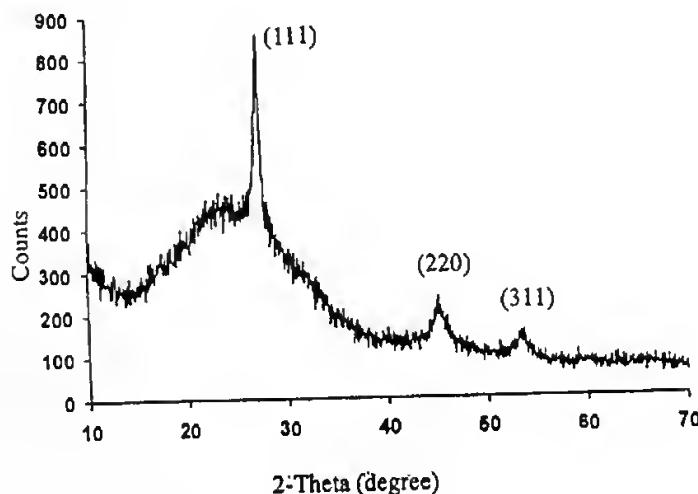


Figure 1. X-ray diffraction pattern for a ZnSe thin film with a thickness of 300 nm, substrate temperature 180°C.

average sizes of the crystallites of the films were determined from FWHM ($b_{2\theta}$) of the XRD spectrogram using the Scherrer's formula [8]

$$D = 0.99\lambda / b_{2\theta} \cos \theta \quad (1)$$

Where $b_{2\theta}$ is full width at the half maximum of [111] peak of XRD pattern and λ is the wave length of the incident X-ray. The average crystallite sizes was found in the range between 200 and 300 Å. The crystallite size increases with increasing film thickness and substrate temperature during deposition. Moreover, heat treatment after film deposition also shows an increase of the crystallite size.

3.2. Optical properties :

The thermally deposited ZnSe films showed high transmittivity to visible light. Figure 2 illustrate the transmission spectra for a ZnSe film before and after heat treatment. The experiments showed that transmission coefficient strongly depends on the film structure, which is determined by the film thickness and its deposition conditions. It was observed that for the heat treated sample the transmission coefficient is greater than the value obtained before the heat treatment. This fact is probably due to the increase in crystallite size. The crystalline boundaries contain structural defects, impurities etc. These factors might influence the absorption process.

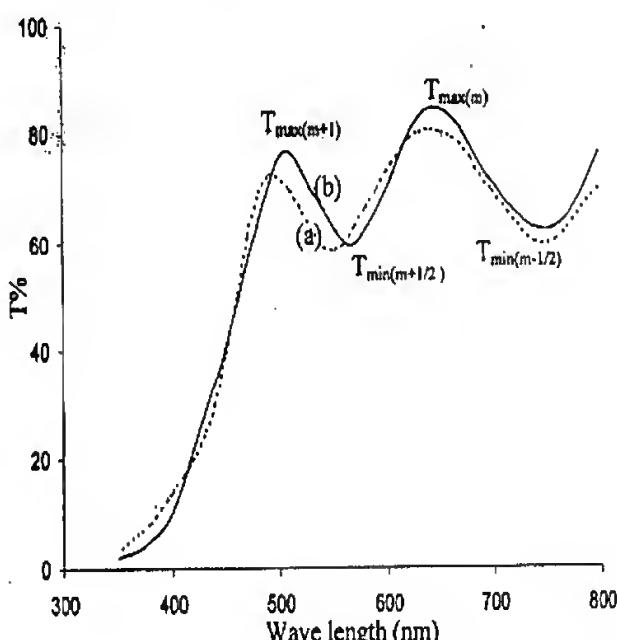


Figure 2. The transmission spectra for a ZnSe film with $t = 380$ nm, $T_s = 180^\circ\text{C}$, (a) before and (b) after the heat treatment.

The number of the interference fringes in the transmission curves is determined by the thickness of the film. For the comparatively thick films, the refractive index, in the spectral domain of the medium and strong transmission, is calculated using the Swanpoel method [9] of creating envelopes of the interference maxima and minima. Firstly an approximate value of refractive index (say, n) is calculated using the expression [9]

$$n = \left[N + (N^2 - n_s^2)^{1/2} \right]^{1/2} \quad (2)$$

where $N = 2n_s(T_{\max} - T_{\min})/T_{\max}T_{\min} + (2n_s^2 + 1)/2$ and n_s is the refractive index of the substrate used. In this last expression T_{\max} and T_{\min} are the transmission maximum and minimum at the same wavelength (λ).

With this value of the refractive index of the film, the 'order' m of the different extremes of the transmission curve is determined with the equation for interference fringes

$$2nt = m\lambda \quad (3)$$

In our case the thickness of the film, t , was known.

The values of m are then approximated to the close integer (for maxima) or half integer (for minima) m_0 [10]. These values of m_0 are used to determine the new value of the refractive index n from the same relation (3). In the interference free zone the refractive index were obtained by extrapolation of the refractive index obtained in the interference zone using Cauchy dispersion rule

$$n = A + B/\lambda^2. \quad (4)$$

Nearly at the absorption edge the absorption coefficient can be calculated from transmittance (T) using the expression [6]

$$\alpha = I/t \ln(I/T). \quad (5)$$

The extinction coefficient (k) is estimated from the value of α and λ using the formula

$$k = \alpha\lambda/4\pi. \quad (6)$$

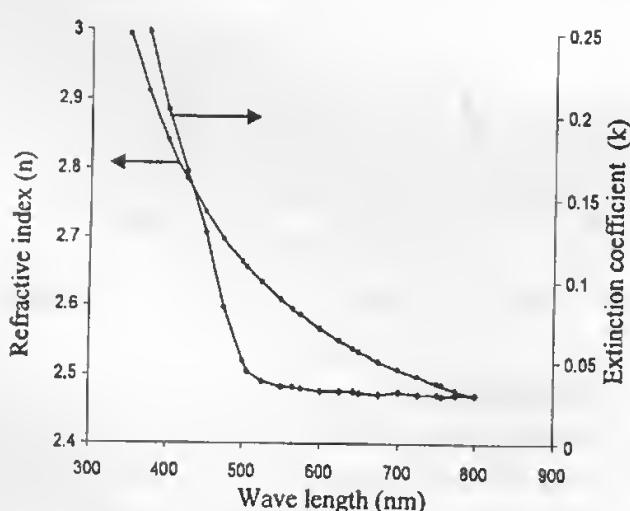


Figure 3. Variation of refractive index (n) and extinction coefficient (k) with wave length of a vacuum deposited ZnSe film, $t = 380$ nm, $T_s = 180^\circ\text{C}$.

Figure 3 illustrates the dependence of n and k of a typical ZnSe film on wave length. Table 1 summarized the calculated values of n , α and k of a typical ZnSe film at selected wave lengths in the interference region.

Table 1. Value of refractive index, absorption coefficient and extinction coefficient of a typical film ($T_s = 180^\circ\text{C}$) of thickness 380 nm at selected wavelengths.

λ (nm)	n_1	m	m_0	n	$\alpha (10^4 \text{ cm}^{-1})$	k
756 (min)	2.407	2.42	2.5	2.487	49.034	0.0295
643 (max)	2.409	2.82	3	2.538	62.567	0.0320
564 (min)	2.4185	3.26	3.5	2.597	76.620	0.0344
505 (max)	2.447	3.68	4	2.658	108.49	0.0436

The fundamental absorption occurred due to allowed direct transitions may be described by the well known relation [11],

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (7)$$

where $h\nu$ is the incident photon energy, E_g represents the energy bandgap and A is characteristic parameter. The analysis of our experimental data shows that for all samples the dependences of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$, indicates the direct nature of fundamental band-to-band transitions. The plot of $(\alpha h\nu)^2$ against $h\nu$ for a few typical are shown in Figure 4. The values of bandgap width, E_g , have been determined by extrapolating the linear portions of the respective curves to $(\alpha h\nu)^2 = 0$. For the investigated

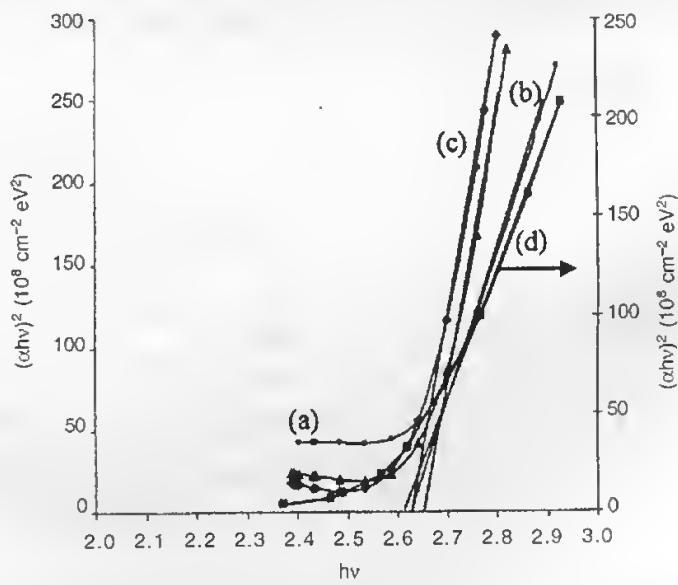


Figure 4. The $(\alpha h\nu)^2$ vs photon energy $h\nu$ plots for a few heat-treated ZnSe films (a) $T_s = 80^\circ\text{C}$, $t = 220$ nm, (b) $T_s = 130^\circ\text{C}$, $t = 205$ nm, (c) $T_s = 180^\circ\text{C}$, $t = 235$ nm and (d) $T_s = 180^\circ\text{C}$, $t = 380$ nm.

samples these values ranged between 2.6 and 2.7 eV, which is in good agreement with the earlier reported values [5, 12, 13]. The transmittance and optical band gap of a few ZnSe films prepared at different substrate temperatures (T_s) are represented in Table 2.

Table 2. Some optical parameters of a few ZnSe films.

Film	Substrate Temperature	Thickness (nm)	Transmittance %	Band gap (eV)
ZnSe (annealed)	80°C	220	63%	2.63
ZnSe (annealed)	130°C	205	74%	2.66
ZnSe (annealed)	180°C	235	70%	2.63
ZnSe (annealed)	180°C	380	70%	2.61

3.3. Electrical properties :

The as grown films were found to be highly resistive and their conductivity at room temperature was in the order of $10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ similar to the values reported by earlier workers [13]. The electrical behaviour of as deposited ZnSe films were found to be unstable. The resistivity of the films decreased with increase of substrate temperature upto 180°C. After deposition, the films were subjected to a heat treatment in vacuum, consisting of several heating and cooling cycles up to a temperature of 250°C and there after found stable. The resistivity of the films were found to slowly decrease with time showing again effect and became nearly stable after about 7 days when kept in dry air or in vacuum. Doping of the films enhanced conductivity considerably. The plots of $\ln\sigma$ vs $1000/T$ (Figure 5) for all the films show a nearly linear dependence with two slopes within the temperature range of 25°C to 120°C.

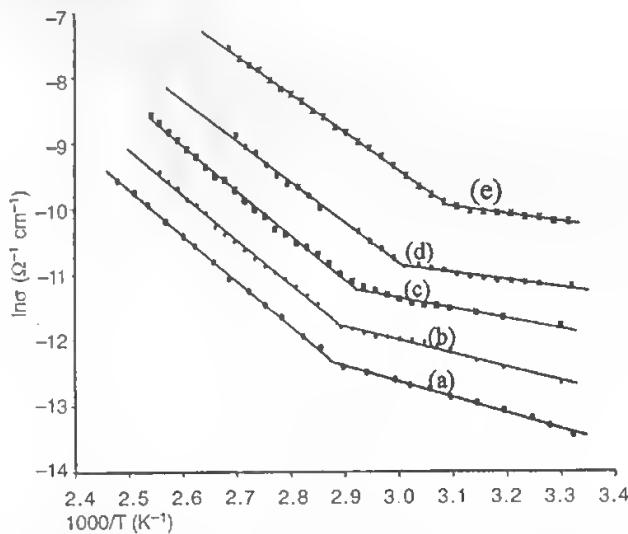


Figure 5. $\ln\sigma$ vs T^{-1} plots of ZnSe films (a) undoped, $T_s = 80^\circ\text{C}$, $t = 220 \text{ nm}$, (b) undoped, $T_s = 130^\circ\text{C}$, $t = 205 \text{ nm}$, (c) undoped, $T_s = 180^\circ\text{C}$, $t = 235 \text{ nm}$, (d) Al doped, $T_s = 180^\circ\text{C}$, $t = 225 \text{ nm}$ and (e) Cu doped, $T_s = 180^\circ\text{C}$, $t = 215 \text{ nm}$.

The temperature dependence of electrical conductivity can be described by

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (8)$$

here, E_a is the thermal activation energy.

Table 3. Values of electrical conductivity and activation energy of a few ZnSe films.

Film	Sub temp (T_s) °C	Conductivity Ohm ⁻¹ cm ⁻¹	Sheet resistivity (10 ⁹) ohm cm ⁻¹	Activation energy eV	
				Range 1	Range 2
ZnSe	80	6×10 ⁻⁷	71	0.207	0.602
ZnSe	130	2×10 ⁻⁶	23	0.176	0.59
ZnSe	180	5×10 ⁻⁶	17	0.137	0.5876
ZnSe:Al	180	1.4×10 ⁻⁵	3.17	0.098	0.536
ZnSe:Cu	180	1.8×10 ⁻⁵	2.86	0.099	0.506

In the low temperature range the lower value of activation energy is attributed to electron hopping among the localized donor states. The values of activation energies (E_a) up to the temperature 120°C corresponds to different impurity levels due to excess zinc in case of undoped films and different dopants for doped films. The Table 3 shows the conductivity and activation energy of a few undoped and doped ZnSe films.

4. Conclusions

ZnSe thin films obtained by vacuum evaporation onto glass substrates at higher temperatures show the polycrystalline nature of the films. The crystallites are preferentially oriented with (111) plane parallel to the substrate surface. The shape of the transmission spectra is strongly influenced by the preparation conditions of films and heat treatment. The spectral dependence of the refractive index indicates a normal dispersion. The values of energy gap, calculated from the absorption spectra, range between 2.6 and 2.7 eV. The as grown ZnSe films were found to be highly resistive and the resistivity was found to decrease with increase of substrate temperature and heat treatment. Doping of the films enhanced the electrical conductivity considerably. From variation of conductivity with temperature, two activation processes were observed for all the films corresponding to two temperature regions.

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